

# The dual melting curves and metastability of carbon tetrachloride

Vern E. Bean and Sharrill D. Wood

National Bureau of Standards, Washington, D.C. 20234  
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Carbon tetrachloride has three known solid phases at atmospheric pressure: Ia (face-centered cubic), Ib (rhombohedral), and II (monoclinic). Both Ia and Ib melt directly at temperatures some 5 K apart. These phase changes have been traced as a function of hydrostatic pressure up to 350 MPa. Between atmospheric pressure and 100 MPa,  $\text{CCl}_4$  has dual melting curves; one for Ia, and a few degrees higher, one for Ib. The two curves diverge with increasing pressure. Above 100 MPa it was not possible to detect the Ia phase. There appears to be no Ia-Ib-liquid triple point. The metastability associated with these phases is discussed.

## INTRODUCTION

Carbon tetrachloride ( $\text{CCl}_4$ ) is a fascinating substance.

It has been reported in the literature<sup>1-7</sup> that, upon cooling at atmospheric pressure,  $\text{CCl}_4$  solidifies at about 245 K into a face-centered cubic crystal structure (the Ia phase) and then transforms to a rhombohedral structure (the Ib phase) with further cooling. When heated, Ib melts around 250 K without passing back through the Ia phase. Should the cooling be limited so that only Ia is formed, then Ia melts around 245 K. Thus, at atmospheric pressure,  $\text{CCl}_4$  has two melting points some 5 K apart. There is also a phase transition from the rhombohedral to a monoclinic structure (the II phase) at atmospheric pressure and 225 K. The Ia phase has been described by investigators working at atmospheric pressure but since the work at higher pressures has been above 273 K, the Ia phase does not appear in phase diagrams reported in the literature.<sup>8-12</sup> We have studied these phase changes as a function of hydrostatic pressure up to 350 MPa using differential thermal analysis (DTA).

## EXPERIMENTAL APPARATUS

The atmospheric pressure data were obtained using a simple variable temperature bath; the high pressure data were obtained using a sample cell adapted to conventional commercial high pressure equipment. First let us consider the bath.

### Atmospheric pressure apparatus

The atmospheric pressure apparatus is a variable temperature circulating bath constructed by cutting appropriate holes into 5 cm thick styrofoam sheets and bonding the various layers together with epoxy. Essentially the bath is a laminated block of styrofoam with three 20 cm deep vertical holes along a common line spaced 9 cm between centers. The center hole is 7.5 cm in diameter and is lined with a thin-wall brass tube which is sealed at the bottom. The other two holes are 3.7 cm in diameter; one is for the sample and the other for a propeller to circulate the fluid. All three holes are interconnected by cross bores at the bottom and near the top. In the styrofoam layers containing the cross bores, the center hole has been enlarged to about 12 cm

in diameter to provide a flow path around the brass tube. Ethanol was used as the circulating fluid.

Cooling was provided by placing crushed dry ice in the brass tube. Cooling rates could be controlled by the amount of dry ice used and the degree of contact with the walls. With this arrangement, temperatures as low as 210 K could be obtained. Heating was obtained simply by removing the dry ice and could be accelerated by blowing a jet of warm air into the brass tube.

Both the propeller and the sample tube were mounted in corks fitted in the tops of their respective holes.

Temperature measurements were made using a copper-Constantan differential thermocouple with a reference junction in an ice bath. The thermocouple was calibrated using a standard platinum resistance thermometer and had a measurement uncertainty of  $\pm 0.12$  K (three times the standard deviation of the residuals from the calibration equation).

The sample tube had a total length of 17 cm. The top 12 cm was a 1.27 cm diameter stainless steel tube, 0.0127 cm wall thickness, used to support the temperature gradient between the sample and the room. This tube was soldered to a thick walled copper test tube, 5 cm long, 1.27 cm in diameter with a 0.64 cm bore 3.2 cm deep, designed to minimize the temperature gradients over the length of the sample. The atmospheric pressure data were obtained using 1.6 g of  $\text{CCl}_4$  with the thermocouple immersed into the  $\text{CCl}_4$ .

### High pressure apparatus

The pressure system was assembled from commercially available equipment including a hand pump, an intensifier, and a pressure vessel having an internal cylindrical volume 2.5 cm in diameter by 7 cm long. Pressure was measured with a bourdon tube gage which was calibrated using a piston gage. The estimated uncertainty in pressure measurement was  $\pm 0.7$  MPa. The pressurizing fluid was a 50/50 mixture of pentane and aviation instrument oil.

The sample was mounted on the pressure vessel closure plug as sketched in Fig. 1. One side of the sample cell was a disk made of 0.05 mm thick brass shim stock and provided with a fill port which was sealed with

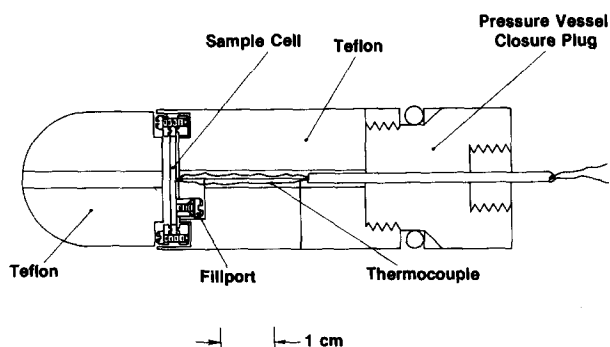


FIG. 1. Diagram of the DTA sample cell mounted on the pressure vessel closure plug.

an "O" ring and a screw. One junction of the differential thermocouple was soldered to the center of the brass disk and the other junction was approximately 2 cm away from the cell but still in the high pressure environment. The other side of the sample cell was a disk made of 0.1 mm thick flexible polyester film mounted in a slack condition to provide a hydrostatic pressure environment for the sample. These two disks were separated by a nylon ring which also provided the seal when the assembly was clamped together with the two brass clamping rings and 12 screws. The sample cell was secured to the pressure vessel closure plug by means of a Teflon mount. Voids on the pressure vessel were filled with Teflon to reduce the effects of adiabatic heating in the pressurizing fluid.

The sample cell contained approximately 0.3 g of  $\text{CCl}_4$ . All samples were taken from the same new bottle of Eastman Kodak Spectro ACS  $\text{CCl}_4$  without additional purification.

Temperatures of the controlled bath for the pressure vessel were measured using a platinum resistance thermometer (PRT) located in a well in a block of brass anchored to the outside of the pressure vessel. The PRT was calibrated with the standard platinum resistance thermometer and the estimated uncertainty in temperature measurement of the PRT is  $\pm 0.13$  K.

The high pressure apparatus was designed only to detect the phase changes. Numerous heat leaks prohibit any estimate of the heat involved in the transitions.

## RESULTS AND DISCUSSION

The relative shape and amplitude of the DTA signals from the formation of the Ia and Ib phases change little in the pressure range investigated. The signals are very different in character making identification of the

TABLE II. Equations for transition temperatures upon decreasing pressure. The general equation is of the form

$$T = A_0 + A_1P + A_2P^2,$$

where  $T$  is the temperature in K and  $P$  is the pressure in MPa.

Transition	$A_0$ K	$A_1$ $\text{K}(\text{MPa})^{-1}$	$A_2$ $\text{K}^2(\text{MPa})^{-2}$	Standard deviation K
II $\rightarrow$ Ib	225.05	0.230	$-4.13 \times 10^{-6}$	0.44
Ib $\rightarrow$ Liquid	249.58	0.386	$-2.18 \times 10^{-4}$	0.54
Ia $\rightarrow$ Liquid	244.63	0.336	$-3.88 \times 10^{-4}$	0.33

two phases a simple matter. The Ia trace has a rise time on the order of several seconds. The peak height of Ib is three times larger than the peak height of Ia if Ib is formed from Ia. However, if Ib is formed directly from the liquid, its peak height is a factor of 6 greater than that of the Ia phase. The rise time for Ib is very short, and it may well be that the rise time of the signal from the formation of Ib approaches the response time of the strip chart recorder. The abrupt nature of this transition makes one think of a coiled spring being released. The character of the Ib trace is the same whether Ib is formed from Ia or directly from the liquid and whether at atmospheric or at high pressure. The nature of these traces is very similar to those reported by Kotake *et al.*<sup>3</sup> The abrupt nature of the liquid Ib transition is also discussed by Morrison and Richards<sup>5</sup> and Badiali *et al.*<sup>6</sup>

### Atmospheric pressure data

The temperatures at atmospheric pressure for the Ia and Ib melting points and the II  $\rightarrow$  Ib transition in this work are listed in Table I along with those from the literature. These temperatures were obtained by least-squares fitting a second-order polynomial in pressure to all of the temperature and pressure data pertaining to a given transition and then evaluating that polynomial at atmospheric pressure. The equations are listed in Table II.

In the atmospheric pressure experiments, the liquid  $\rightarrow$  Ia and Ib  $\rightarrow$  II transitions occurred at rather well defined temperatures, 246.3 and 223.2 K, respectively, in contrast to the wide range of transition temperatures obtained by Badiali *et al.*,<sup>6</sup> who used very small samples.

The Ia  $\rightarrow$  Ib transition is unusual. In experiments wherein Ia was continuously cooled, Ib has been observed to spontaneously form at temperatures over the range of 245.0 to 234.7 K. Ib has been formed from Ia in experiments wherein the melting temperature of Ia was being sought and at the temperature where the Ia melt was expected. Morrison and Richards<sup>5</sup> reported having the same experience. In another experiment the liquid was cooled to within a fraction of a degree of the liquid  $\rightarrow$  Ia transition and then the stopper of sample tube was given a sharp rap with a wooden pencil; Ib formed immediately without first passing through Ia. A rap with the pencil when the sample is in the Ia phase will also result in immediate transformation to Ib. The Ia phase appears to be completely metastable with respect to the Ib phase.

TABLE I. Transition temperatures (K).

II $\rightarrow$ Ib	Ib $\rightarrow$ liquid	Ia $\rightarrow$ liquid	Ref.
226.6	247.8	244.8	1
...	250.28	245.70	4
$225.7 \pm 0.1$	$250.53 \pm 0.01$	$246.00 \pm 0.01$	5
225.4	250.4	245.5	6
226.0	249.9	245.6	14
$225.05 \pm 0.57$	$249.58 \pm 0.50$	$244.63 \pm 0.54$	This work

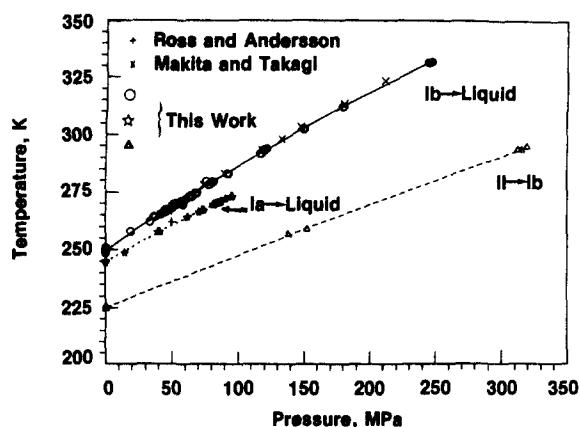


FIG. 2. Curves for the Ib → liquid, Ia → liquid, and II → Ib transitions.

### Dual melting curves and metastability

Figure 2 is a plot of the two melting curves and the II → Ib phase line which were obtained by decreasing the pressure at constant temperatures. Equations representing these curves are listed in Table II. Below 273 K and 100 MPa there are dual melting curves, one for Ia and, a few degrees higher, one for Ib. Above 100 MPa, there is only one melting curve, that of Ib.

These two curves diverge with increasing pressure. The Ia curve was followed in the directions of both increasing and decreasing temperature and pressure. At a given temperature, the rate of pressure increase is a determining factor whether the Ia or the Ib phase is formed. To obtain Ia, it is necessary to gently increase the pressure as the freezing point is approached such that the thermodynamic state of the  $\text{CCl}_4$  suffers minimal perturbation. Typically, once the pressure was within about 15 MPa of the expected Ia freezing point, the pressure was slowly increased by increments of 0.7 MPa with 6–8 min delay between increases. The curves of Fig. 2 were obtained using similar pressure decreases.

Figure 3 is a plot of the freezing and melting curves that have been fitted by least squares to both the Ia and Ib data in the region where the Ia phase exists. A word

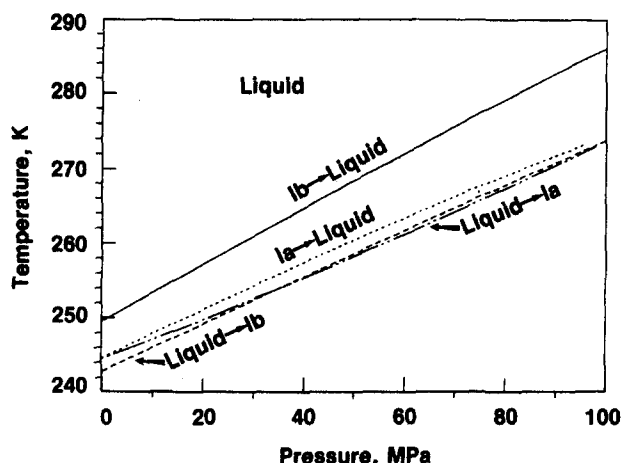


FIG. 3. Melting and freezing curves for Ia and Ib.

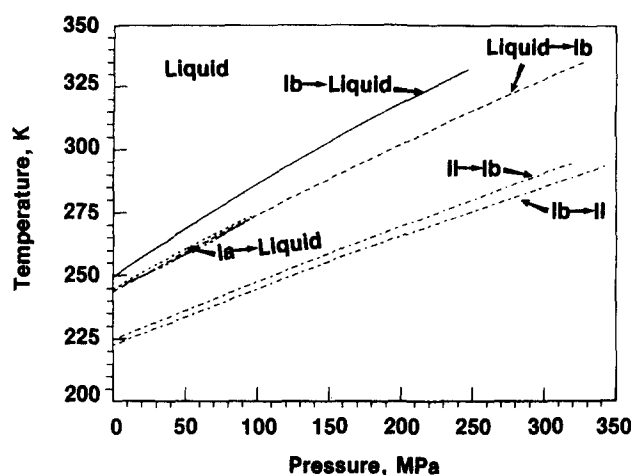


FIG. 4. Curves for the Ib → liquid, liquid → Ib, II → IB, and Ib → II transitions.

of caution must be given regarding the Ib freezing curve: the data for this curve include pressure and temperature values from both the liquid → Ib and the Ia → Ib transitions. These data are widely scattered due to the metastable nature of these transitions so the curve represents only a qualitative average of the Ib formation data.

At 272.1 K, the DTA trace for the liquid → Ia transition was quite normal. At 273.1 K, the trace had become rounded with a slower rise time and lower amplitude. Above 273.7 K, it was not possible to obtain the Ia phase.

The space between the melting and freezing curves for Ia is rather convex, narrowing down to a gap of only 2.1 MPa at 273.1 K. The evidence indicates that the Ia freezing curve and hence the Ia melting curve simply end in the neighborhood of 273 K and 100 MPa and that there is no Ia–Ib–liquid triple point. The fact that when Ib is formed from Ia by increasing the pressure and then, upon decreasing the pressure, melts directly without passing back through Ia and the fact that we are dealing with metastable states indicate that there should be no triple point.

It is premature to regard 273 K and 100 MPa as the unique end point on the Ia melting line. The formation of the Ia phase may well depend upon sample purity, sample size, the material from which the sample cell is made, the rate of change of temperature and pressure, and sample history. Careful attention to these details may make it possible to extend the end of the Ia melting curve to a higher temperature and pressure. Ross and Andersson<sup>11</sup> reported one experimental point on the Ia melting curve as is indicated in Fig. 2.

The data of Makita and Takagi,<sup>13</sup> which cover the range between 278 and 323 K, are in excellent agreement with the Ib melting curve as shown in Fig. 2. The lower limit of their work is 5 K above the end of the Ia line; they did not report seeing the Ia phase. Again Ross and Andersson<sup>11</sup> reported one experimental point on the Ib curve which is plotted in Fig. 2.

Figure 4 is an expansion of Fig. 3 to include all our measurements of freezing and melting and the Ib → II and

II-Ib phase lines. From Figs. 3 and 4 we note the following. (1) All of the phase lines are concave toward the  $P$  axis with the exception of the liquid-Ia line which is concave away from the  $P$  axis. (2) The liquid-Ib and Ib-liquid curves diverge with increasing pressure. (3) The Ib-II and II-Ib curves also diverge with increasing pressure.

Finally, it is important to recall that Badiali *et al.*<sup>6</sup> have shown that the degree of metastability at atmospheric pressure is a function of sample size. This feature would be expected to continue into the high pressure region. The curves presented here are from samples that are large compared to those of Badiali and thus do not define the limits of metastability.

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